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Stable isotopes ($\delta^{18}O$ and $\delta^{13}C$), trace and minor element compositions of Recent scleractinians and Last Glacial bivalves at the Santa Maria di Leuca deep-water coral province, Ionian Sea

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ABSTRACT

The aragonitic skeletons of bathyal cold-water corals have a high potential as geochemical *in situ* archives for paleoceanography. Oxygen isotopes and stable carbon isotopes ($\delta^{18}O$ and $\delta^{13}C$) have been analyzed, as well as trace and minor element compositions (e.g. Mg/Ca, Sr/Ca, U/Ca, B/Ca and P/Ca) in *Lophelia pertusa*, one of the most important frame-builders at the Santa Maria di Leuca (SML) deep-water coral hotspot in the Central Mediterranean. The Apulian Bank is swept by strong currents of the Adriatic Deep Water Outflow. The temperature of 13.9 °C is the highest temperature recorded for *L. pertusa* and provides an important end-member of environmental conditions for geochemical analyses on living Atlantic and Mediterranean cold-water corals. Temperature and salinity (38.77 PSU) are stable throughout the year, and thus virtually no changes should be observed in the stable oxygen isotope signal—if the coral precipitates its skeleton in equilibrium with seawater. We measured various marine properties, such as the seawater oxygen isotope composition ($\delta^{18}O_{sw}$), stable carbon isotope composition ($\delta^{13}C_{DIC}$) of dissolved inorganic carbon (DIC), and dissolved inorganic nutrient concentrations (PO_4, NO_3, NO_2, NH_3 and SiO_2). Bottom water at the coral sites shows a mean oxygen isotope composition of 1.47‰ $\delta^{18}O_{sw}$-VSMOW, and $\delta^{13}C_{DIC}$ showed a mean of 1.1‰ VPDB.

A section of a living *L. pertusa* with a thick theca calcification was probed with a Merchantek MicroMill at a high spatial sampling resolution with 10 samples per 1 mm. This reduced the signal-smoothing inherent to conventional sampling. The $\delta^{18}O_{ag}$ of coral aragonite ranges between −2.0‰ and +2.8‰ VPDB and the $\delta^{13}C_{ag}$ ranges between −7.77‰ and +1.47‰ VPDB. The Gaussian data distribution for both parameters, including heavy equilibrium values, suggests the completeness of the captured isotopic variability. The strict linear correlation of $\delta^{13}C$ and $\delta^{18}O$ displays a strong 'kinetic' vital effect. The intercept of the $\delta^{13}C/\delta^{18}O$ correlation line with the $\delta^{13}C_{DIC}$-composition permits recognition of $\delta^{18}O$ equilibrium values of aragonite and thus reconstruction of water temperatures *despite* strong disequilibrium precipitation. Since the environmental parameters (T, S and $\delta^{18}O_{sw}$) are stable, the entire isotopic signal of the coral must be driven by biological fractionation and might reflect growth speed variations, potentially related to pH variations and changes in the saturation state of the calcifying fluid or seasonally varying nutrient availability.

Laser ablation tracks show a trace element composition dependent to microstructural zones (fibrous aragonite vs. centres of calcification). The parabolic relation of the classical temperature proxies Mg/Ca and U/Ca point to trace element vital effects, rendering them unreliable in *L. pertusa*. The P/Ca ratio shows similar values as *Desmophyllum dianthus*, for which a linear dependence with seawater phosphate (DIP) has been previously demonstrated. Consequently *L. pertusa* might be an additional nutrient recorder at bathyal depths. From the same site we also analysed the stable isotopic composition

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of the Last Glacial pectinid bivalve *Pseudamussium peslutrae*, which has been radiocarbon-dated (AMS-^{14}C) at 26.3 ka ^{14}C yr BP. The isotope values of the shell calcite document a strongly differing glacial temperature–salinity regime preceding the Holocene coral growth above a prominent hiatus.

1. Introduction

Cold-water corals receive an increasing interest as geochemical archives in the deep sea, as their aragonitic skeletons provide *in situ* recorders for numerous proxies for the reconstruction of changing deep-water composition and past circulation patterns. The feasibility of highly precise radiometric dating, which can yield insights into past bathyal reservoir ages and ventilation rates, adds to the interest. Many investigations of the oxygen isotopes and stable carbon isotopes have been carried out in the North Atlantic, which unequivocally documented a strong biological fractionation superimposed on environmental signals (e.g., Mikkelsen et al., 1982; Swart, 1983; Freiwald et al., 1997; Mortensen and Rapp, 1998; Smith et al., 2000; Spiro et al., 2000; Adkins et al., 2003; Rollion-Bard et al., 2003; Blamart et al. 2005; Lutringer et al., 2005; Risk et al., 2005). Smith et al. (1997) showed that the linear trend of δ^{18}O and δ^{13}C from biological fractionation can be used to reconstruct mean annual temperatures (lines technique), while the intra-annual variability is overprinted by biological fractionation. The magnitude of these vital effects and their triggering mechanisms are still debated (Adkins et al., 2003).

Trace element investigations on the cold-water coral *Desmophyllum dianthus* by Montagna et al. (2006) revealed a linear correlation between the seawater phosphate concentration (DIP) and the P/Ca-ratio in the coral skeleton, which allows reconstruction of the past seawater nutrient concentrations.

Fossil cold-water corals are widely distributed across the Mediterranean Basin (Taviani et al., 2005a; McCulloch et al., in preparation), but living specimens have only been reported from few sites with particular oceanographic settings (Taviani et al., 2005a, b; Schembri et al., 2007; Freiwald et al., 2009). The Apulian Bank (Fig. 1) is one of these Mediterranean areas that host lush Recent coral gardens (Tursi et al., 2004; Taviani et al., 2005a; Freiwald et al., 2009). Here the Adriatic Outflow Water (Manca et al., 2006) descends across the Apulian Bank, forming a young bottom-water mass, in contact with the overlying Levantine Intermediate Water. The strong bottom currents force resuspension of sediment and a low light transmissivity is typical for this turbulent zone.

In the present study we document the stable isotope and trace element composition of Recent cold-water corals (*Lophelia pertusa* and *D. dianthus*) and a Last Glacial bivalve (*Pseudamussium peslutrae* (= *P. septemradiatum*)). Important for the interpretation of the geochemical signatures is the knowledge of geochemical parameters of the water column. The APLABES and HERMES-projects produced a wealth of CTD-data (Fig. 2) and collected

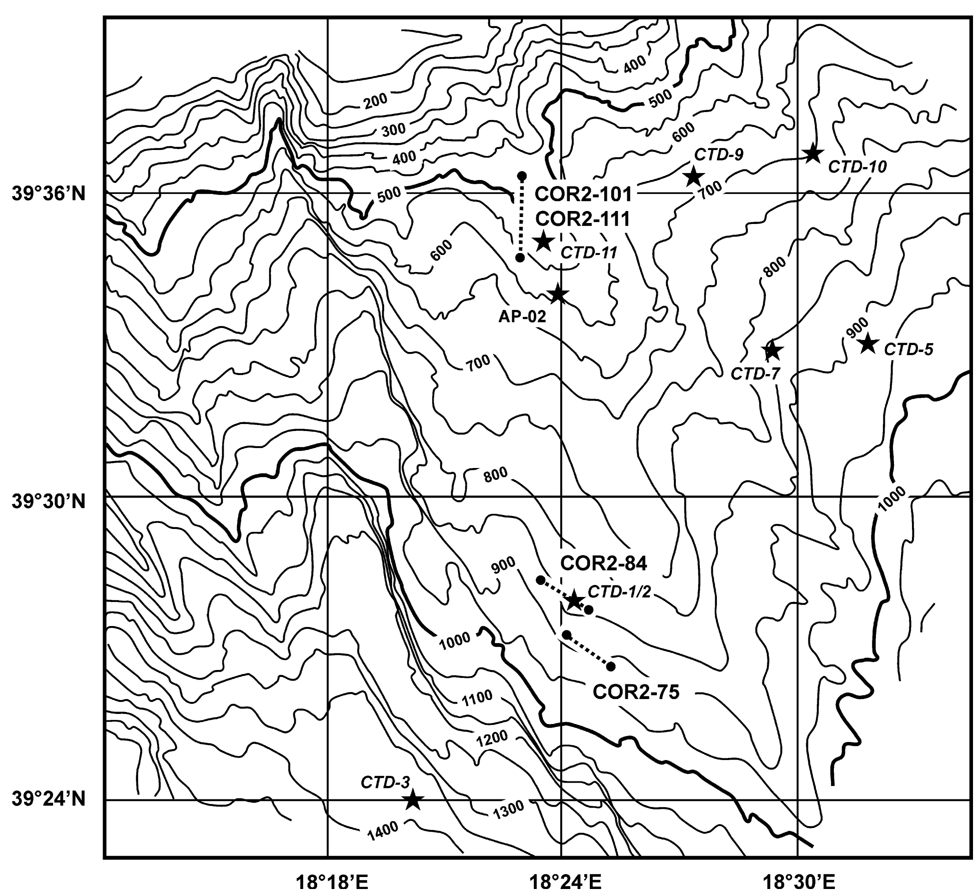

Fig. 1. Simplified bathymetry of the research area on the Apulian Bank south of Santa Maria di Leuca. Dredging sites for the geochemically analyzed Recent cold-water corals are indicated, as well as CTD sites (stars) for seawater isotopy (CTD-1 to 11) and nutrient composition (AP-02). The bathymetry is based on the multibeam-mapping carried out by the FIRB-APLABES project.